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**METHOD FOR THE REMOVAL OF NO_x AND N₂O FROM THE RESIDUAL GAS
IN NITRIC ACID PRODUCTION**

[Verfahren zur Beseitigung von NO_x and N₂O aus dem
Restgas der Salpetersaeureproduktion]

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Method for the Removal of NO_x and N₂O from the Residual Gas in NitricAcid ProductionSpecification

The invention concerns a method for removing NO_x and N₂O from the residual gas of nitric acid production.

An exhaust gas, which is loaded with nitric oxide NO, nitrogen dioxide NO₂ (together called NO_x), as well as laughing gas N₂O is produced during the industrial production of nitric acid HNO₃ by means of the catalytic combustion of ammonia. While NO and NO₂ have long been known as compounds with ecologically toxic relevance (acid rain, smog formation) and limits have been fixed worldwide for their maximum allowable emissions, also laughing gas has come to an increasing extent into the focus of environmental protection in the last few years, since it contributes to a considerable extent to the degradation of stratospheric ozone and to the greenhouse effect.

After the reduction of laughing gas emissions in the adipic acid industry, it is the nitric acid production that presents the greatest source of industrial laughing gas emissions. There is therefore an urgent need, due to reasons of environmental protection, to find technical solutions to achieve a reduction of laughing gas emissions together with NO_x emissions in nitric acid production.

There are numerous method variations (identified herein as DeNO_x step), such as chemical washes, adsorption methods, or catalytic reduction methods for the removal of NO_x from the exhaust gas of nitric acid production. An overview is provided in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 17, VCH Weinheim (1991) (D1). It should be emphasized that the selective catalytic reduction (SCR) of NO_x by means of ammonia to N₂ and H₂O can run at temperatures

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of between approx. 150°C and approx. 450°C, depending on the catalyst, and makes possible a NO_x degradation of more than 90%. It is the most widely used variation of the NO₂ reduction in nitric acid production, but also does not lead to a reduction of N₂O gas, like the other variations.

For this purpose is necessary a special second catalytic step according to the current state of the art, which is combined in a suitable way with the DeNO_x step.

This consideration, for examples, constitutes the basis of a method described in US patent 5,200,162, which claims the decomposition of N₂O into an exhaust gas, which likewise contains NO_x, downstream from a DeNO_x step. A partial flow of the exhaust gas, which exits the N₂O decomposition step, is therein usually cooled and fed back into it in order to prevent an overheating of this step due to the exothermic reaction of the N₂O decomposition. The invention

concerns exhaust gases with a N_2O content of up to 35% by volume, that is, for example, in exhaust gases of the adipic acid production.

A method presented by Shell describes the integrated removal of NO_x and N_2O from residual gas of the nitric acid production (Clark, D. M.; Maaskant, O. L.; Crocker, M., The Shell De NO_x System: A Novel and Cost Effective NO_x Removal Technology as Applied in Nitric Acid Manufacture and Associated Processes, presented at Nitrogen '97, in Geneva, February 9-11, 1997 (D2)).

The Shell reactor system is based on a so-called lateral flow reactor principle, wherein the De NO_x step already functions with relatively low temperatures (starting at 120°C). In order to remove N_2O is used an amorphous metallic oxide catalyst.

In an arrangement of corresponding catalysts in the residual gas, which exits the absorption tower at a temperature of $20\text{-}30^\circ\text{C}$, the window of possible working temperatures is predetermined by the operating temperature of the residual gas turbine.

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The residual gas turbine should namely be operated, from the technical and economic point of view of the overall process, at the most advantageous inlet temperatures of $< 550^\circ\text{C}$ and the highest possible ΔT and Δp .

This is especially important for the removal of N_2O , since clearly higher temperatures than during the catalytic reduction of NO_x

are required for this purpose according to the current state of the art. The economy of this option is therefore linked to a sufficient catalyst activity.

An overview of the numerous catalysts, whose suitability for the decomposition and reduction of laughing gas has been demonstrated in principle, is provided in Kaptejin, F.; Rodriguez-Mirasol, J.; Moulijn, J. A., Appl. Cat. B: Environmental 9 (1996) 25-64 (D3).

As particularly suitable for the decomposition of N_2O appear to be, among others, the metal exchanged zeolite catalysts (US patent 5,171,533).

The zeolites used herein are produced by ion exchange in an aqueous solution containing metallic salts. For the ion exchange are used metals of the group consisting of: copper, cobalt, rhodium, iridium, ruthenium, or palladium. The copper zeolites are very sensitive to water vapor and their activity is rapidly reduced under these conditions (M.; Sandoval, V. H.; Schweiger, W.; Tissler, A.; Turek, T., Chemie Ingenieur Technik (Chemical Engineering Technology) 70 (1998) 878-882 (D5)), while the other metals listed herein are relatively cost intensive.

Only a 20% degradation of N_2O was achieved with an iron-doped zeolite of the Fe-ZSM-5 type under conditions corresponding to those described in Table 1 of US 5,171,533, in the absence of NO_x , H_2O and O_2 at 450°C.

In the case of Fe-ZSM-5, its activity for the degradation of N_2O in the presence of corresponding amounts of NO is however clearly increased, which is caused by a reaction under formation of NO_2 according to $\text{NO} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{NO}_2$, which is catalyzed by Fe-ZSM-5

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(Kapteijn, F.; Marban, G.; Rodriguez-Mirasol, J.; Moulijn, J. A., Journal of Catalysis 167 (1997) 256-265 (D6); Kapteijn, F.; Mul, G.; Marban, G.; Rodriguez-Mirasol, J.; Moulijn, J. A., Studies in Surface Science and Catalysis 101 (1996) 641-650 (D7)).

A higher activity than in the corresponding Fe-zeolites was detected in the presence of NO_x for Cu- or Co-exchanged zeolites.

In the descriptions presented in the state of the art (D6, D7) for the degradation of N_2O in the presence of a Fe-ZSM-5 catalyst at 400°C were usually utilized equimolar amounts of NO and N_2O . According to D6 and D7, the effect of NO_x on the N_2O degradation increases constantly with a decreasing NO/ N_2O ratio, so that with a NO/ N_2O ratio of less than 0.5, the N_2O degradation is no longer satisfactory.

The best results are observed with a mol ratio of NO/ N_2O of 1 or greater than 1.

When a catalyst such as this is used for N_2O reduction in the exhaust gas of the nitric acid production, the NO_2 formed in the process could be fed back, according to the authors, for the recovery

of HNO_2 . The NO_x and N_2O concentrations in the exhaust gas are herein at approx. 1000 ppm, depending on the method variation.

Zeolites containing iron based on ferrierite for the reduction of gases containing N_2O are the object of WO 99/34901. The catalysts utilized herein contain 80-90% of ferrierite as well as further binding fractions. The water proportion of the gases to be reduced is within the range of 0.5 to 5%. In a comparison of different zeolite types, the best results were achieved (97% N_2O degradation at 375°C and $\text{NO}/\text{N}_2\text{O} = 1$) with zeolites of the FER (ferrierite) type with the degradation of N_2O at temperatures of 375 to 400°C . A considerably lower degradation was observed with the use of zeolites of the pentasil (MFI) or mordenite (MOR) type. In MFI zeolites containing iron, it was only possible to reach a maximum N_2O degradation of 62% even under the above conditions.

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With regard to the known state of the art, the object becomes thus to make available an economic method, in particular for the HNO_2 production, which makes possible, aside from a high NO_x degradation, also a satisfactory N_2O degradation.

Good results for the N_2O degradation are also achieved especially with a substoichiometric $\text{NO}_x/\text{N}_2\text{O}$ ratio, especially with a ratio of < 0.5 , preferably of < 0.1 , such as those that result after a reduction of the NO_x content.

The invention attains the object and concerns a method for reducing the NO_x and N_2O concentration of the residual gas from the nitric acid production, wherein the residual gas that exits the absorption tower is guided through a combination of two steps before entering into the residual gas turbine, the NO_x content in the gas is reduced in the first step (De NO_x step), and the N_2O content in the gas is reduced in the second step (De N_2O step), the $\text{NO}_x/\text{N}_2\text{O}$ ratio before entering the second step is within a range of between 0.001 and 0.5, preferably within a range of between 0.001 and 0.02, especially within a range of between 0.01 to 0.1, and this gas is brought into contact with a catalyst in the second step, which contains essentially one or several zeolites loaded with iron.

The catalysts used according to the invention contain essentially preferably > 50% by weight, especially > 70% by weight, of one or several zeolites loaded with iron. In this way, for example, aside from a Fe-ZSM-5 zeolite, a further zeolite containing iron, such as, for example, a zeolite containing iron of the MFI or MOR type, can be contained in the catalyst utilized according to the invention. The catalyst utilized according to the invention can also contain other additives, for example, binding agents, which are known to persons skilled in the art.

The catalysts used for the De NO_2O step are preferably based on zeolites in which the iron was incorporated by means of a solid ion

exchange. The work is usually started with the commercially available ammonium zeolites (for example, $\text{NH}_4\text{-ZSM-5}$) and the corresponding iron salts (for example, $\text{FeSO}_4 \times 7 \text{ H}_2\text{O}$), and these are intensively mixed with each other by mechanic means in a ball mill at room temperature (Turek et al; Appl. Catal. 184 (1999) 249-256; EP-A-0,955,080). Reference is especially made to these publications. The obtained catalyst powders are then calcined in the air in a chamber kiln at temperatures within a range between 400 and 600°C. After calcining, the Fe zeolites are intensively washed in distilled water and dried after the zeolite is filtered. The Fe zeolites obtained in this way are finally mixed with the suitable binding agents and extruded, for example, as cylindrical catalyst elements. As binding agents are suitable all of the usually utilized binders, which are usually aluminum silicates, such as kaolin.

According to the invention, the zeolites that can be used are loaded with iron. The iron content can amount to up to 25% with reference to the mass of zeolite, preferably however 0.1 to 10%. Zeolites of the MFI, BETA, FER, MOR and/or MEL type are especially suitable. Exact data with regard to the design or structure of these zeolites are provided in the Atlas of Zeolite Structure Types, Elsevier, 4th revised edition, 1996, to which reference is expressly herein. Zeolites preferred according to the invention are of the MFI

(pentasil) or MOR (mordenite) type. Zeolites of the Fe-ZSM-5 type are especially preferred.

According to the invention, the DeN_2O catalysts are arranged in such a way in combination with a DeNO_x step upstream thereof between the absorption tower and the residual gas turbine that the residual gas exiting the absorption tower is first guided at temperatures of $< 400^\circ\text{C}$, especially $< 350^\circ\text{C}$, into a reactor (first step), in which the NO_x content is reduced to up to < 100 ppm (refer to Figure 2). The operating pressure of this first step is preferably at 1 to 15 bar, especially 4 to 12 bar.

The upstream DeNO_x step corresponds to a method for reducing the NO_x emissions usually utilized in nitric acid plants corresponding to

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the state of the art. The NO_x content of the residual gas must be sufficiently high, however, so that the cocatalytic effects of NO or NO_2 can become effective in the downstream DeN_2O step connected.

With the operation of the DeN_2O step without upstream DeNO_x , that is, with an inlet flow with approximately equimolar amounts of NO and N_2O , a feedback of the NO_2 formed according to $\text{NO} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{NO}_2$ in the HNO_3 process is not economical because of the relatively low NO_2 concentration of < 2000 ppm.

The N_2O content of the gas remains essentially unchanged in the DeNO_x step. In this way, the gas usually has a NO_x content of 1 to

200 ppm after exiting the first step, preferably 1 to 100 ppm, and especially 1 to 50 ppm, and a N_2O portion of 200 to 2000 ppm, preferably 500 to 1500 ppm. After exiting the $DeNO_x$ step is obtained a NO_x/N_2O ratio of 0.001 to 0.5, preferably 0.001 to 0.2, and especially 0.01 to 0.1. The water content of the gas is usually within the range of between 0.05 and 1%, preferably within the range of between 0.1 and 0.8%, and especially within the range of between 0.1 and 0.5% likewise after exiting the $DeNO_x$ step, as well as also the DeN_2O step.

The residual gas conditioned in this way is now guided into the DeN_2O step connected downstream, where a degradation of the N_2O into N_2 and O_2 is produced utilizing the cocatalytic effect of NO_x in the presence of a corresponding zeolite catalyst.

It was surprisingly discovered that the N_2O degradation is drastically increased in the presence of the zeolite catalysts containing iron utilized according to the invention also in the presence of small amounts of NO_x , that is, with a molar NO_x/N_2O ratio of < 0.5 (refer to the figure). In this way, for example, at $450^\circ C$, a molar NO_x/N_2O ratio of 0.01 is still sufficient according to the invention to reduce the N_2O concentration from 72% to 33% in the presence of a Fe-ZSM-5 catalyst. This is even more surprising because the accelerated N_2O degradation is ascribed in the state of the art to the already mentioned stoichiometric conversion of N_2O with

NO. It appears that with sufficient temperature and low $\text{NO}_x/\text{N}_2\text{O}$ ratio, NO_x assumes the role of a homogeneous cocatalyst, which accelerates the N_2O degradation according to $\text{N}_2\text{O} \rightarrow \text{N}_2 + 1/2 \text{O}_2$. A maximum degradation of N_2O in the downstream De N_2O step is possible with a $\text{NO}_x/\text{N}_2\text{O}$ ratio within the aforementioned limits. As soon as the ratio drops below 0.001, also the N_2O degradation drops to values that are no longer satisfactory (compare with example 5). After exiting the De N_2O step, the content of N_2O is within a range of between 0 and 200 ppm, preferably within a range of 0 to 100 ppm, and especially within a range of 0 and 50 ppm, pursuant to the method according to the invention.

The operating temperature of the De N_2O step is especially determined therein by the desired degree of degradation of N_2O and the amount of NO_x contained in the residual gas, but is dependent to a great extent from the catalyst load, as is known to the persons skilled in the art and as in almost all processes of catalytic exhaust gas purification, that is, it is dependent from the throughput of exhaust gas with reference to the catalyst amount. The operating temperature of the second step is preferably within a range of between 300 and 550°C, especially within a range of between 350 and 500°C, with a pressure within a range of between 1 and 15 bar, especially between 4 and 12 bar. With increasing pressure, the

cocatalytic effect of NO_x on the N_2O decomposition is increased, so that a further reduction of the operating temperature is made possible by increasing the pressure.

In addition, the content of oxygen and H_2O , which can fluctuate within specific limits and can exert an inhibiting effect on the N_2O conversion depending of the mode of operation and the method variant of the nitric acid production, should be taken into consideration when determining or establishing the operating temperature. The O_2 content is within a range of between 1 and 5% by volume, especially within a range of between 1.5 and 4% by volume.

With the zeolite catalysts containing iron, which are utilized according to the invention, can thus be achieved a degradation of N_2O of > 90%, especially > 95%, at temperatures within the range of between 300 and 550°C, preferably between 350 and 500°C. With increasing temperature, it is still possible to achieve a satisfactory N_2O degradation, even with a $\text{NO}_x/\text{N}_2\text{O}$ ratio of 0.01.

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The method according to the invention makes it possible to reduce to a minimum the NO_x and N_2O content of the residual gas of nitric gas production to minimal values by combining a DeNO_x step and a DeN_2O step. By arranging the DeNO_x step ahead of the DeN_2O step and between the absorption tower and the residual gas turbine, the method

according to the invention is also very economic, because of the monotonously increasing temperature profiles.

The process management with the two steps arranged ahead of the decompression turbine is also particularly advantageous, since both steps can be carried out under pressure (depending the HNO_3 method variant between 4 and 11 bar), which induces a reduction of the effectively necessary reactor or catalyst volume.

Through the operation of the DeNO_x step already at relatively low temperatures is also ensured furthermore a sufficient reduction of the NO_x content when the plant is started, for which only a low process heat is available.

A further advantage of the arrangement of these two steps between the absorption tower and the residual gas turbine in a monotonously increasing temperature profile is that the residual gas exiting the combination according to the invention without previous cooling and without provisions for exhaust gas purification can be directly fed to the residual gas turbine for an optimal recovery of compression and heat energy.

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Examples:

DeNO_x Step:

A classic SCR catalyst based on $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ (refer to possibly G. Ertl, H. Knoezinger J. Weitkamp: Handbook of Heterogeneous

Catalysis, Volume 4, pages 1633-1668) connected upstream of the DeN₂O catalyst can be used as DeNO_x catalyst as described, using NH₃ as reduction medium. The latter was operated with a temperature of 350°C. In dependence upon the fed amount of NH₃, different contents of NO_x and therewith NO_x/N₂O ratios were set at the outlet of the DeNO_x step.

DeN₂O Step:

The production of an MFI catalyst containing iron was carried out by means of solid ion exchange, based on a commercially obtainable zeolite in ammonium form (ALSI-PENTA, SM27). Detailed information regarding the preparation can be found in: M. Rauscher, K. Kesore, R. Moennig, W. Schweiger, A. Tissler, T. Turek, Appl. Catal. 184 (1999) 249-256.

The catalyst powders were calcined in the air for 6 hours at 823 K, washed, and dried overnight at 383 K. After adding the corresponding binder followed the extrusion as cylindrical catalyst elements (2 x 2 mm).

The tests were carried out in a stationary operated throughflow apparatus with online analytic at space velocity of respectively 10,000 h⁻¹.

The composition of the feed amounted to:	1000 ppm	NO _x
	1000 ppm	N ₂ O
	0.5% by vol.	H ₂ O

2.5% by vol. O₂

Residue N₂

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By varying the added amount of NH₃, can be obtained the following residual concentrations of NO_x and N₂O:

Example	Added NH ₃ Amount	Resulting NO _x Concentration (after DeNO _x Step at 350°C)	Resulting NO _x /N ₂ O Ratio (after DeNO _x Step)	Resulting N ₂ O Concentration (after DeN ₂ O Step at 475°C)
1	500 ppm	500 ppm	0.5	40 ppm
2	800 ppm	200 ppm	0.2	54 ppm
3	950 ppm	50 ppm	0.05	81 ppm
4	990 ppm	10 ppm	0.01	99 ppm
5	1000 ppm	< 1 ppm	< 0.001	462 ppm

As can be deduced from the above-listed examples, a high N₂O degradation up to a NO_x/N₂O ratio of 0.001, especially 0.01 is possible. If the ratio drops below this limit value, a sufficient degradation is no longer ensured, because of the no longer sufficient cocatalytic function of NO_x.

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Patent Claims:

1. A method for reducing the NO_x and N_2O concentration of residual gas from the nitric acid production, in which the residual gas exiting the absorption tower is guided through a combination of two steps before entering into the residual gas turbine, and the NO_x content is reduced in the first step and the N_2O content is reduced in the second step, the $\text{NO}_x/\text{N}_2\text{O}$ ratio before the gas enters into the second step is within a range of between 0.001 and 0.5 and this gas is brought into contact with a catalyst in the second step, which contains essentially one or several zeolites loaded with iron.

2. The method of claim 1, wherein the zeolite(s) loaded with iron, which is/are contained in the catalyst, is/are of the MFI, BEA, FER, MOR and/or MEL type.

3. The method of claim 2, wherein the zeolite(s) loaded with iron is/are of the MFI type.

4. The method of claim 3, wherein the zeolite is a Fe-ZSM-5.

5. The method of at least one of the preceding claims, wherein the temperature of the first step is $< 400^\circ\text{C}$, preferably $< 350^\circ\text{C}$.

6. The method of at least one of the preceding claims, wherein the temperature of the second step is within a range of between 300 and 550°C , preferably within a range of between 350 and 500°C .

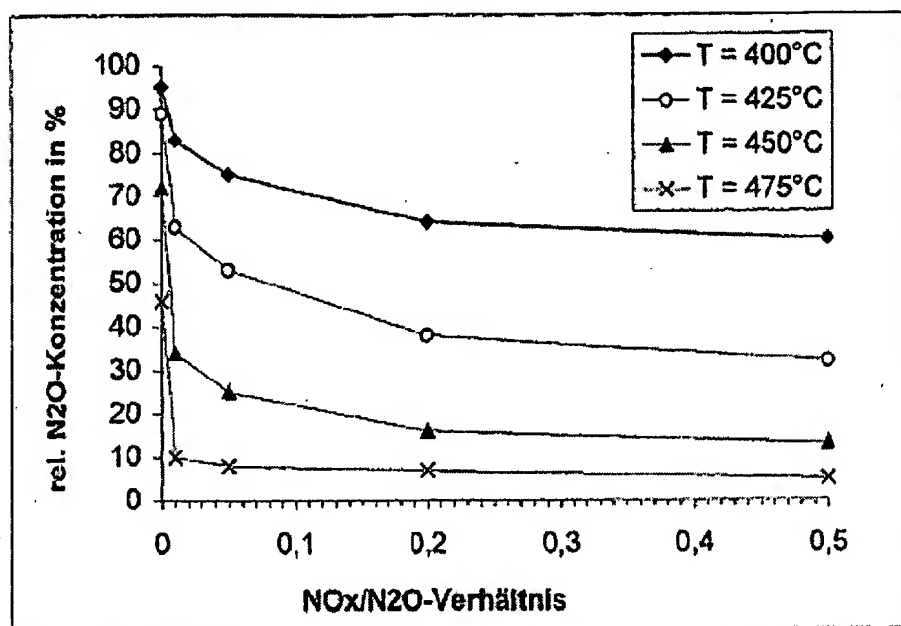
7. The method of at least one of the preceding claims, wherein the two steps are operated at a pressure within the range of between 4 and 12 bar.

8. The method of at least one of the preceding claims, wherein the first step is operated in accordance with the SCR method.

9. The method of at least one of the preceding claims, wherein the water content of the gas after exiting the absorption tower and before entering the first or second step is within a range of between 0.05 and 1% by volume, especially within a range of between 0.1 and 0.8% by volume.

10. The method of at least one of the preceding claims, wherein the gas has a NO_x content within a range of between 1 and 200 ppm and a N_2O content within a range of between 200 and 2000 ppm after exiting the first step, and a NO_x content of 1 to 200 ppm and a N_2O content within a range of between 0 and 200 ppm after exiting the second step.

11. The method of at least one of the preceding claims, wherein a N_2O degradation of > 90%, especially of 95%, is achieved.

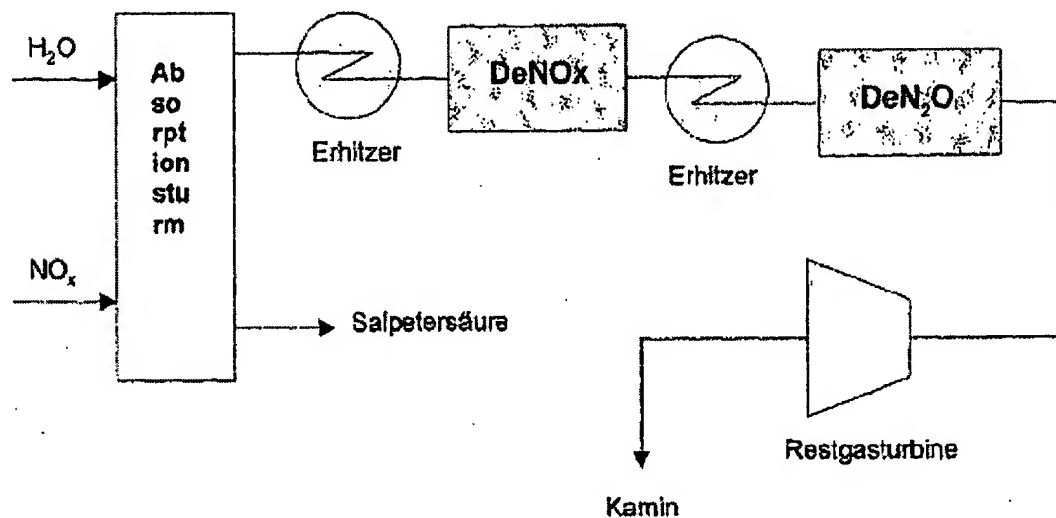


Legends in Fig. 1:

rel. N2O-Konzentration in % = rel. N₂O concentration in %

NO_x/N2O-Verhaeltnis = NO_x/N₂O ratio

Abbildung = Figure



Legends in Fig. 2:

Erhitzer = Boiler

Salpetersaeure = Nitric acid

Kamin = Chimney

Restgasturbine = Residual gas turbine

Abbildung = Figure